

# **PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT**

**NOVEMBER 2002 SAMPLING EVENT**



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## **Pesticide Monitoring Project Report November 2002 Sampling Event**

### ***Executive Summary***

As part of the District's quarterly ambient monitoring program, unfiltered water and sediment samples from 39 sites were collected from November 12 to November 19, 2002, and analyzed for over sixty pesticides and/or products of their degradation. The herbicides 2,4-D, ametryn, atrazine, bromacil, diuron, hexazinone, norflurazon, prometon, and simazine, along with the insecticides/degradates atrazine desethyl, atrazine desisopropyl, endosulfan sulfate, ethoprop, and metalaxyl were detected in one or more of these surface water samples.

The herbicides ametryn, bromacil, and trifluralin together with the insecticides/degradates DDD, DDE, DDT, dieldrin, gamma BHC (lindane), and three PCB compounds were found in the sediment at several locations. One DDT and two DDD compound sediment concentrations were of a magnitude considered to represent significant and immediate hazard to aquatic organisms in coastal sediments. However, there are no corresponding freshwater sediment quality assessment guidelines to further evaluate potential hazards at these particular sampling sites.

The compounds and concentrations found are typical of those expected from intensive agricultural activity.

### ***Background and Methods***

The District's pesticide monitoring network includes stations designated in the Everglades National Park Memorandum of Agreement, the Miccosukee Tribe Memorandum of Agreement, the Lake Okeechobee Operating Permit, and the non-Everglades Construction Project (non-ECP) permit. The District's canals and marshes depicted in Figure 1 are protected as Class III (fishable and swimmable) waters, while Lake Okeechobee is protected as a Class I drinking water supply. Water Conservation Area 1 (WCA1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

With the exception of imidacloprid, sixty-six pesticides and degradation products were analyzed for in samples from all of the 39 sites (Figure 1). The analytes, their respective minimum detection limits (MDL), and practical quantitation limits (PQL) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee Florida. The reader is referred to the *Quality Assurance Evaluation* section of this report for a summary of any limitations on data validity that might influence the utility of these data.

Each pesticide's description and possible uses and sites of application are taken from Hartley and Kidd (1987). The Florida Ground Water Guidance Concentrations (FGWGC) (FDEP, 1994a) are listed to provide an indication at what level these pesticide residues could possibly impact human health, based on drinking water consumption or other routes of exposure (e.g., inhalation, ingestion of food residues, dermal uptake). Primary ground water standards are enforceable

ground water standards, not screening tools or guidance levels. To evaluate the potential impacts on aquatic life, due to the pulsed nature of exposure, the maximum observed concentration is compared to the Criterion Maximum Concentration published by the USEPA under Section 304 (a) of the Clean Water Act, if available, or the lowest EC<sub>50</sub> or LC<sub>50</sub> reported in the summarized literature. Sediment concentrations are compared to coastal sediment quality assessment guidelines (FDEP, 1994b), as there are no corresponding freshwater sediment quality assessment guidelines. A value below the threshold effects level (TEL) should not have an impact on wildlife. The value between the TEL and probable effects level (PEL) has a possibility for impacts, while those exceeding the PEL have a substantial probability for impacting wildlife. This summary covers surface water and sediment samples collected from November 12 to November 19, 2002.

### ***Findings and Recommendations***

At least one pesticide was detected in surface water at 31 of the 39 sites and in sediment at 13 of the 32 sites. Sediment samples are not routinely collected at GORDYRD, CR33.5T, NSIDWC06, and NSIDWC07. Additionally sediment samples were not successfully collected at S177, S332, and S99. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All of these compounds have previously been detected in this monitoring program.

Two DDD and one DDT compound sediment concentrations were of a magnitude considered to represent significant and immediate hazard to aquatic organisms in coastal sediments. However, there are no corresponding freshwater sediment quality assessment guidelines to further evaluate potential hazards at the District's sampling sites.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

### ***Usage and Water Quality Impacts***

2,4-D: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The highest 2,4-D concentration was detected at S4 (4.9 µg/L) (Table 2). Using these criteria, these levels should not have an acute impact on fish or aquatic invertebrates.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > 10 µg/L (Verschuere, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface

solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour  $LC_{50}$  of 14.1 mg/L for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.012 to 0.059  $\mu\text{g/L}$ . Using these criteria, these surface water levels should not have an acute, detrimental impact on fish or aquatic invertebrates. The sediment concentrations ranged from 11 to 39  $\mu\text{g/Kg}$ . However, no sediment quality assessment guidelines have been developed for ametryn.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour  $LC_{50}$  of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210  $\mu\text{g/L}$  for bluegill and fathead minnow (Verschuere, 1983). The atrazine surface water concentrations found in this sampling event at 24 of the 39 sampling locations, ranged from 0.011 to 12  $\mu\text{g/L}$ . Using these criteria, these surface water levels should not have an acute or chronic detrimental impact on fish or invertebrates. Atrazine was not quantified in the sediment.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of ground water discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median  $<0.1$ , occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). Most of the sites fall in this category with the exception of S3. The DAR value of 0.3 suggests that some degradation of atrazine has occurred in this basin. However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the south Florida environment should be made with caution.

BHC, gamma (lindane): Lindane is a chlorinated hydrocarbon insecticide registered for foliar and soil applications on a wide range of crops and public health applications. The U.S. production of lindane was halted in 1976, and all unformulated lindane has been imported since that time. The fate of lindane in aquatic systems will be controlled by the availability of and to biotransformation process. Lindane transformation will be favored in biologically rich, anaerobic environments. Although sorption to suspended sediment and biota is not extensive,

sorption is an important process for ultimately transporting lindane to anaerobic sediments where transformation occurs. Hydrolysis and oxidation do not appear to be important fate process for lindane; data on the photolysis of lindane are contradictory and confusing. Lindane is only slightly bioaccumulated in organisms (Callahan et al. 1979). Sediment quality assessment guidelines have been developed for several metals and organic compounds in coastal sediments (FDEP, 1994b). The only sediment concentration of lindane detected was 0.49 µg/Kg at ACME1DS. This value is between the TEL (0.32 µg/Kg) and PEL (0.99 µg/Kg). At this level, possible impacts to wildlife could occur. However, the reliability of the sediment guidelines developed, only have a low degree of confidence.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC<sub>50</sub> of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at CR33.5T (2.8 µg/L). Using these criteria, these levels should not have an acute or chronic detrimental impact on fish. Bromacil was quantified in the sediment at 54 and 25 µg/Kg at S176 and S355B, respectively. However, no sediment quality assessment guidelines have been developed for bromacil.

DDD, DDE, DDT: DDE is an abbreviation of **dichlorodiphenyldichloroethylene** [2,2-bis(4-chlorophenyl)-1,1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**dichlorodiphenyltrichloroethane**), a popular insecticide for which the USEPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**dichlorodiphenyldichloroethane**), and the high K<sub>oc</sub> of these compounds accounts for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioaccumulation factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

The DDD concentrations detected range from 1.2 to 24 µg/Kg. Any value, which is between the TEL (1.2 µg/Kg) and PEL (7.8 µg/Kg), have the possibility for impacting wildlife. The two values (15 µg/Kg at S6 and 24 µg/Kg at S2) that exceed the PEL are considered to represent significant and immediate hazard to aquatic organisms.

The TEL is 2.1 µg/Kg and the PEL is 374 µg/Kg for DDE in coastal sediments. All but one (1.6 µg/Kg at G94D) of the DDE concentrations detected (2.8 to 130 µg/Kg) are between the TEL and PEL. The levels between the TEL and PEL have the possibility for impacting wildlife as they have exceeded the threshold level, while the one concentration below the TEL should not impact wildlife.

One of the DDT concentration's detected (7.8 µg/Kg at S2) exceeds the PEL (4.8 µg/Kg). This level is considered to represent a significant and immediate hazard to aquatic organisms.

Dieldrin: Dieldrin is a non-systemic insecticide with all uses canceled in the United States. The

high  $K_{oc}$  and low water solubility accounts for dieldrin's affinity for sediment. The hydrophobicity of this compound also results in a significant bioconcentration factor and the potential for a high degree of accumulation in aquatic organisms (Table 4). Dieldrin is highly toxic to mammals. Sediment quality assessment guidelines developed for dieldrin in coastal sediments determined a PEL of 4.3  $\mu\text{g/Kg}$  (FDEP, 1994b). The concentration detected in the sediment at S7 (5.8  $\mu\text{g/Kg}$ ) is above this level and at this concentration is usually or always associated with adverse biological effects. No dieldrin was detected in the surface water.

Diuron: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96-hour  $\text{LC}_{50}$  of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48 hour  $\text{LC}_{50}$  of 1.4 mg/L for water fleas and a 96 hour  $\text{LC}_{50}$  of 0.7 mg/L for water shrimp (Verschuere, 1983). Most algal effects occur at concentrations  $> 10 \mu\text{g/L}$  (Verschuere, 1983). The highest surface water concentration of diuron found during this sampling event was 4.4  $\mu\text{g/L}$  (Table 2). Using these criteria, this level should not have an acute, harmful impact on fish or algae. Diuron was not detected in the sediment.

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's constant indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Lyman et al., 1990). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). The only surface water detection occurred at S178 (0.046  $\mu\text{g/L}$ ). However, no FDEP surface water standard (FAC 62-302) has been promulgated for endosulfan sulfate.

Ethoprop: Ethoprop is a non-systemic soil insecticide/nematicide used on many crops including potatoes, tomatoes, sugarcane and turf. Environmental fate and toxicity data in Tables 4 and 5 indicate that ethoprop (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is moderately toxic to mammals and relatively non-toxic to fish; and (3) does not bioconcentrate significantly. Aquatic invertebrate  $\text{LC}_{50}$  toxicity ranges from 13  $\mu\text{g/L}$  to 25.3  $\mu\text{g/L}$  for ethoprop (U.S. Environmental Protection Agency, 1985). The highest surface water concentration of ethoprop found in this sampling event was 0.18  $\mu\text{g/L}$  at S4. This concentration is below a level that would have an acute detrimental impact on fish or aquatic invertebrates.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an  $\text{EC}_{50}$  of 145 mg/l for *Daphnia magna* (U.S. Environmental Protection Agency, 1988). The highest surface water concentration detected in this sampling event at S191 (0.098  $\mu\text{g/L}$ ) should not have an acute impact on fish or aquatic

invertebrates.

Metalaxyl: Metalaxyl is a systemic fungicide. Registered uses include potatoes, strawberries, citrus, avocados and vegetables. Environmental fate and toxicity data in Tables 4 and 5 indicate that metalaxyl (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metalaxyl detected was 0.13 µg/L at S191 (Table 2). Using these criteria, the concentrations of metalaxyl detected should not have an acute, harmful impact on fish or aquatic invertebrates.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC<sub>50</sub> for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.027 to 0.74 µg/L. Even at the highest concentration, this is over an order of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates.

PCBs: Polychlorinated biphenyls (PCBs) is the generic term for a group of 209 congeners that contain a varying number of substituted chlorine atoms on one or both of the biphenyl rings. PCB-1016, PCB-1221, and PCB 1254 are commercial grade mixture containing 16%, 21%, and 54%, respectively, chlorine by weight. Production of PCBs was banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily sorbed to suspended sediments due to the very low solubility in water (Callahan et al., 1979). The tendency of PCBs for adsorption increases with the degree of chlorination and with the organic content of the adsorbent. While the production ban, phase out of uses, and stringent spill clean-up requirements have significantly reduced environmental loadings in recent years, the persistence and tendency to accumulate in sediment and bioaccumulate in fish, make this class of organochlorine compounds especially problematic. Florida sediment quality assessment guidelines have been developed for total PCBs in coastal sediments (FDEP, 1994b). However, an evaluation of the reliability of the sediment quality assessment guidelines for total PCBs suggests a low degree of confidence can be placed on these guidelines due to the insufficient data used in their development. The TEL is 21.6 µg/Kg and the PEL 189 µg/Kg for PCB's. The sediment residues detected all fall between the TEL and PEL which therefore have a possibility for impacting wildlife. None of the PCB congeners were detected in the surface water.

Prometon: Prometon is a non-selective systemic herbicide registered for use in non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that prometon (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The highest concentration of prometon detected (0.033 µg/L at NSIDC07) is several orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates. Prometon was not detected in

the sediment.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC<sub>50</sub> of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 µg/L (Verschueren, 1983). Aquatic invertebrate LC<sub>50</sub> toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. Environmental Protection Agency, 1984). The highest surface water concentration of simazine detected at CR33.5T (7.3 µg/L) was below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

Trifluralin: Trifluralin is a selective pre-emergent herbicide used for the control of annual grasses and broad-leaved weeds in a variety of row crops including cabbage and corn. Environmental fate and toxicity data in Tables 4 and 5 indicate that trifluralin (1) is strongly sorbed to soil and therefore can accumulate in sediment; (2) is relatively non-toxic to mammals and moderately toxic to fish; and (3) does have the potential to bioconcentrate significantly. Sediment quality assessment guidelines could not be developed for trifluralin in coastal sediments due to insufficient data (FDEP, 1994b). No trifluralin was detected in the surface water.

### ***Quality Assurance Evaluation***

Replicate samples were collected at sites S355B, S190, S79, and FECSR78. All the analytes detected in the surface water had precision ≤ 30% RPD. No analytes were detected in the field blanks collected at S18C, S79, G123, and S6. No pesticide analytes were detected in the equipment blanks performed at S38B, S18C and S99. All collected samples were shipped and all bottles were received.

Low concentrations of representative analytes from each pesticide group/method were added to laboratory water as well as to samples submitted. Matrix spike recoveries for cypermethrin did not meet the specified requirements for the water samples collected at the following locations: S190 (including replicates), L3BRS, S8, S7, G123 (including field blank), S142, and S140. The remainder of the analytes for each sample adhered to the targets for precision and accuracy as outlined in the FDEP Comprehensive Quality Assurance Plan. Organic quality assurance targets are set according to historically generated data or are adapted from the U.S. Environmental Protection Agency with slight modifications or internal goals, based on FDEP limited data. Parameters with low or high recoveries indicate that the sample matrix interferes with these analyses and interpretation of the respective analytical results should consider this effect.

### ***Glossary***

LD<sub>50</sub>: The dosage which is lethal to 50% of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LC<sub>50</sub>: A concentration which is lethal to 50% of the aquatic animals tested within a short



(acute) exposure period, usually 24 to 96 hours.

EC<sub>50</sub>: A concentration necessary for 50% of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

Koc: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:

The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:

The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

MDL: The minimum concentration of an analyte that can be detected with 99% confidence of its presence in the sample matrix.

PQL: The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQL is further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15%. In general, the PQL is 2 to 5 times larger than the MDL.

TEL: The threshold effects level represents the upper limit of the range of sediment contaminant concentrations dominated by no effect data entries, or the minimal effects range. Within this range, concentrations of sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms

PEL: The probable effects level was calculated to define the lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects or the lower limit of the probable effects range. Within the probable effects range, concentrations of sediment-associated contaminants are considered to represent significant and immediate hazards to aquatic organisms.

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# SFWMD Pesticide Monitoring Network



## LEGEND

- Sample Location
- Citrus Crops
- Sugar Crops
- Truck Crops

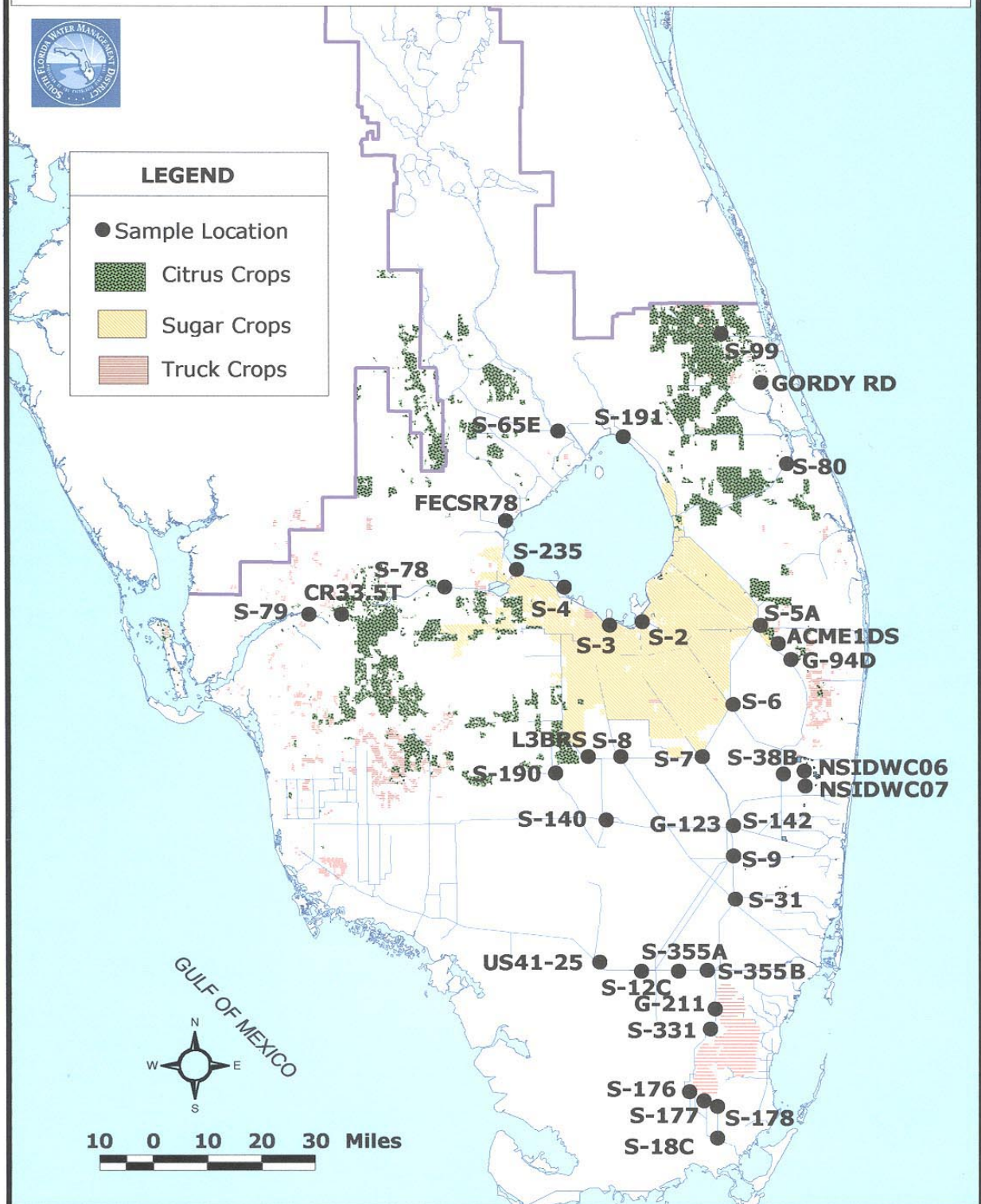


Table 1. Minimum detection limits (MDL) and practical quantitation limits (PQL) for pesticides determined in November 2002.

Pesticide or metabolite	Water: range of MDL-PQL (µg/L)	Sediment: range of MDL-PQL (µg/Kg)	Pesticide or metabolite	Water: range of MDL-PQL (µg/L)	Sediment: range of MDL-PQL (µg/Kg)
2,4-D	0.8 - 3.2	14 - 560	endosulfan sulfate	0.0032 - 1.36	0.72 - 28.8
2,4,5-T	0.8 - 3.2	14 - 560	endrin	0.019 - 0.8	1.4 - 56
2,4,5-TP (silvex)	0.8 - 3.2	14 - 560	endrin aldehyde	0.0042 - 0.176	0.72 - 28.8
alachlor	0.047 - 0.192	22 - 880	ethion	0.019 - 0.8	1.8 - 72
aldrin	0.0019 - 0.08	0.36 - 14.4	ethoprop	0.019 - 0.8	3.6 - 144
ametryn	0.0094 - 0.4	1.8 - 72	fenamiphos (nemacur)	0.028 - 1.2	14 - 560
atrazine	0.0094 - 0.4	1.8 - 72	fonofos (dyfonate)	0.019 - 0.8	3.6 - 144
atrazine desethyl	0.0094 - 0.4	N/A	heptachlor	0.0023 - 0.096	0.36 - 14.4
atrazine desisopropyl	0.0094 - 0.4	N/A	heptachlor epoxide	0.0019 - 0.08	0.36 - 14.4
azinphos methyl (guthion)	0.019 - 0.8	1.8 - 72	hexazinone	0.019 - 0.8	7.2 - 288
α-BHC (alpha)	0.0021 - 0.088	0.43 - 17.2	imidacloprid	N/A	N/A
β-BHC (beta)	0.0032 - 0.136	0.36 - 14.4	linuron	0.2 - 0.48	7.2 - 140
δ-BHC (delta)	0.0019 - 0.08	0.72 - 28.8	malathion	0.028 - 1.2	5.4 - 216
γ-BHC (gamma) (lindane)	0.0019 - 0.08	0.36 - 14.4	metalaxyl	0.047 - 2	N/A
bromacil	0.038 - 1.6	14 - 560	methamidophos	N/A	18 - 720
butylate	0.019 - 0.8	N/A	methoxychlor	0.0098 - 0.4	1.8 - 72
carbophenothion (trithion)	0.015 - 0.64	1.8 - 72	metolachlor	0.057 - 2.4	18 - 720
chlordane	0.019 - 0.8	5.4 - 216	metribuzin	0.019 - 0.8	3.6 - 144
chlorothalonil	0.015 - 0.64	1.8 - 72	mevinphos	0.057 - 3.2	7.2 - 288
chlorpyrifos ethyl	0.019 - 0.8	1.8 - 72	mirex	0.011 - 0.48	1.4 - 56
chlorpyrifos methyl	0.0094 - 0.4	3.6 - 144	monocrotophos (azodrin)	N/A	36 - 1440
cypermethrin	0.019 - 0.8	1.8 - 72	naled	0.075 - 3.2	29 - 1160
DDD-P,P'	0.0045 - 0.192	0.72 - 28.8	norflurazon	0.019 - 0.8	3.6 - 144
DDE-P,P'	0.0038 - 0.16	0.72 - 28.8	parathion ethyl	0.019 - 0.8	5.4 - 216
DDT-P,P'	0.0038 - 0.16	1.1 - 44	parathion methyl	0.019 - 0.8	5.4 - 216
demeton	0.11 - 4.8	36 - 1440	PCB	0.019 - 0.8	7.2 - 640
diazinon	0.019 - 0.8	3.6 - 144	permethrin	0.015 - 0.64	2.2 - 88
dicofol (kelthane)	0.042 - 1.76	5.4 - 216	phorate	0.028 - 1.2	1.8 - 72
dieldrin	0.0019 - 0.08	0.36 - 14.4	prometryn	0.019 - 0.8	5.4 - 216
disulfoton	0.019 - 0.8	3.6 - 144	prometon	0.019 - 0.8	N/A
diuron	0.2 - 0.48	7.2 - 140	simazine	0.0094 - 0.96	1.8 - 72
α-endosulfan (alpha)	0.0038 - 0.16	0.36 - 14.4	toxaphene	0.094 - 4	27 - 1080
β-endosulfan (beta)	0.0038 - 0.16	0.36 - 14.4	trifluralin	0.0075 - 0.32	1.4 - 56
			zinc phosphate	0.50 - 2	N/A

N/A - not analyzed

Table 2. Summary of pesticide residues (µg/L) above the method detection limit found in surface water samples collected by SFWMD in November 2002.

Date	Site	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	atrazine desisopropyl	bromacil	diuron	endosulfan sulfate	ethoprop	hexazinone	metalaxyl	norflurazon	prometon	simazine	Number of compounds detected at site
11/12/2002	S12C	Y	-	-	0.011 I	-	-	-	-	-	-	-	-	-	-	-	1
	S176	N	-	-	0.016 I	-	-	-	-	-	-	-	-	-	-	-	1
	S177	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S178	N	-	-	-	-	-	-	-	0.046	-	-	-	-	-	-	1
	S18C	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S331	N	-	-	0.018 I	-	-	-	-	-	-	-	-	-	-	-	1
	S332	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S355A	N	-	-	0.014 I	-	-	-	-	-	-	-	-	-	-	-	1
	S355B	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	US41-25	Y	-	-	0.014 I	-	-	-	-	-	-	-	-	-	-	-	1
11/13/2002	G123	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	L3BRS	Y	-	0.016 I	-	-	-	-	-	-	-	-	-	0.027 I	-	0.016 I	3
	S140	N	-	-	-	-	-	0.16	-	-	-	-	-	0.14	-	0.073	3
	S142	N	-	0.013 I	-	-	-	-	-	-	-	-	-	-	-	-	1
	S190	N	-	-	-	-	0.019 I *	-	0.39 I *	-	-	-	-	0.074 I *	-	0.87 *	4
	S31	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S7	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S8	N	-	0.026 I	0.062	0.012 I	-	-	-	-	-	-	-	-	-	-	3
	S9	Y	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
11/14/2002	ACME1DS	N	-	0.032 I	0.078	-	-	-	-	-	-	0.020 I	-	-	-	-	3
	G94D	N	-	0.031 I	0.074	-	-	-	-	-	-	0.020 I	-	-	-	-	3
	NSIDWC06	N	-	0.012 I	0.44	-	-	-	4.4	-	-	-	-	-	-	-	3
	NSIDWC07	N	-	0.023 I	1.1	-	-	-	-	-	-	-	-	-	0.033 I	-	3
	S38B	N	-	0.015 I	0.80	0.090	-	-	-	-	-	-	-	-	0.023 I	-	4
	S5A	N	-	0.021 I	0.16	-	-	-	-	-	-	0.024 I	-	-	-	0.010 I	4
	S6	N	-	0.056	0.14	-	-	-	-	-	-	0.025 I	-	-	-	-	3
11/18/2002	C25S99	N	-	-	-	-	-	-	-	-	-	0.079	-	0.61	-	0.035 I	3
	GORDYRD	Y	-	-	-	-	-	-	-	-	-	-	-	0.26	-	0.027 I	2
	S2	N	-	0.021 I	0.12	0.016 I	-	-	-	-	-	-	-	-	-	-	3
	S3	N	-	-	0.10	0.025 I	-	-	-	-	-	-	-	-	-	0.010 I	3
	S4	N	4.9	0.018 I	1.4	0.085	-	-	0.35 I	-	0.18	0.026 I	-	0.18	-	0.19	9
	S80	N	-	-	0.044	-	-	-	-	-	-	-	-	0.24	-	0.12	3
11/19/2002	CR33.5T	Y	-	-	12	1.0	-	2.8	0.56	-	-	-	-	0.74	-	7.3	6
	FECSR78	Y	-	-	0.031 I *	-	-	-	-	-	-	0.066 I *	-	-	-	-	2
	S191	N	-	-	0.015 I	-	-	0.042 I	-	-	-	0.098	0.13 I	-	-	-	4
	S235	Y	1.3 I	0.059	0.58	0.031 I	-	-	-	-	0.027 I	-	-	0.18	-	0.20	7
	S65E	Y	-	-	0.047	-	-	-	-	-	-	-	-	-	-	-	1
	S78	Y	-	-	0.22	0.019 I	-	-	-	-	-	-	-	0.065 I	-	-	3
	S79	Y	-	-	0.56 *	0.036 I *	0.030 I	-	0.86 *	-	-	-	-	-	-	0.50 *	5
Total number of compound detections			2	13	24	9	2	3	5	1	2	8	1	10	2	12	

N - no Y - yes R - reverse; - denotes that the result is below the MDL; \* - results are the average of duplicate samples

I - value reported is less than the minimum quantitation limit and greater than or equal to the minimum detection limit

Table 3. Summary of pesticide residues ( $\mu\text{g/Kg}$ ) above the method detection limit found in sediment samples collected by SFWMD in November 2002.

Date	Site	Flow	ametryn	bromacil	DDD-P,P'	DDE-P,P'	DDT-P,P'	dieldrin	BHC, gamma (lindane)	PCB-1016	PCB-1221	PCB-1254	trifluralin	Number of compounds detected at site
11/12/2002	S176	N	-	54 l	-	-	-	-	-	-	-	-	15 l	2
	S355B	N	-	25 l	-	-	-	-	-	-	-	-	-	1
11/13/2002	S7	N	-	-	-	-	-	5.8	-	-	-	180	-	2
11/14/2002	ACME1D	N	-	-	1.2 l	4.6	-	-	0.49 l	-	-	-	-	3
	G94D	N	-	-	-	1.6 l	-	-	-	-	-	-	-	1
	S38B	N	-	-	1.7 l	4.6	-	-	-	-	-	-	-	2
	S5A	N	-	-	3.8 l	8.2	1.7 l	-	-	-	-	-	-	3
	S6	N	11 l	-	15	47	4.3 l	-	-	-	-	-	-	4
11/18/2002	S2	N	18 l	-	24	130	7.8 l	-	-	-	-	-	-	4
	S3	N	-	-	2.8 l	9.8	-	-	-	-	-	-	-	2
	S4	N	39 l	-	7.7 l	25 l	-	-	-	-	-	-	-	3
11/19/2002	FECSR78	Y	-	-	-	2.8 l	-	-	-	-	22 l	-	-	2
	S79	Y	-	-	-	-	-	-	-	98.5 l *	-	-	-	1
Total number of compound detections			3	2	7	9	3	1	1	1	1	1	1	

- denotes that the result is below the MDL; \* - results are the average of duplicate samples

l - value reported is less than the minimum quantitation limit and greater than or equal to the minimum detection limit

Table 4. Selected properties of pesticides found in November 2002 sampling event.

common name	Surface Water Standards 62-302 (µg/L)	Ground Water Guidance Conc. (µg/L)	LD50 acute rats oral (mg/kg) (1)	EPA carcinogenic potential	Water Solubility (mg/L) (2, 3)	Koc (mL/g) (2, 3)	soil half-life (days) (2, 3)	SCS rating (2)			Bioconcentration Factor (BCF)
								LE	SA	SS	
2,4-D (acid)	(100)	70**	375	D	890	20	10	M	S	M	13
ametryn	-	63	1110	D	185	300	60	M	M	M	33
atrazine	-	3**	3080	C	33	100	60	L	M	L	86
bromacil	-	90	5200	C	700	32	60	L	M	M	15
DDD, p,p'	-	0.1	3400	-	0.055	239900	-	-	-	-	3173
DDE, p,p'	-	0.1	880	-	0.065	243220	-	-	-	-	2887
DDT, p,p'	0.001	0.1	113	-	0.00335	140000	-	-	-	-	15377
dieldrin	0.0019	0.1	37 - 87	B2	0.14	10000 est.	-	-	-	-	1873
diuron	-	14	3400	D	42	480	90	M	M	L	75
endosulfan sulfate	-	0.3	-	-	0.117	-	-	-	-	-	2073
ethoprop	-	-	62	-	750	70	25	L	S	M	15
hexazinone	-	231	1690	D	33000	54	90	L	M	M	2
metalaxyl	-	420	669	-	7100	100	70	L	M	M	4
norflurazon	-	280	9400	C	28	700	90	M	M	L	94
PCB's	0.014	0.5**	-	B2	-	-	-	-	-	-	-
prometon	-	105	2980	-	720	200	500	L	M	M	15
simazine	-	4**	>5000	C	6.2	130	60	L	M	M	221
trifluralin	-	5	>10000	C	0.3	8000	60	S	L	M	1219

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS)

Volatility from water: R = rapid, I = insignificant, S = significant

Bioconcentration Factor (BCF) calculated as  $BCF = 10^{(2.791 - 0.564 \log WS)}$  (4)

B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)

FDEP surface water standards for Class III waters except Class I in ( )

\*\* primary standard

(1) Hartley, D. and H. Kidd. (Eds.) (1987). The Agrochemicals Handbook. Second Edition, The Royal Society of Chemistry. Nottingham, England.

(2) Goss, D. and R. Wauchope. (Eds.) (1992). The SCS/ARS/CES Pesticide Properties Database: II Using It With Soils Data In A Screening Procedure. Soil Conservation Service. Fort Worth, TX.

(3) Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsea, MI.

(4) Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. (1990). Handbook of Chemical Property Estimation Methods. American Chemical Society, Washington, DC.

(5) U.S. Environmental Protection Agency (1996). Drinking Water Regulations and Health Advisories. Office of Water. EPA 822-B-96-002.



Table 5. Toxicity of pesticides found in the November 2002 sampling event to freshwater aquatic invertebrates and fishes (ug/L).

common name	48 hr EC50 Water flea <i>Daphnia magna</i>	acute toxicity (*)	chronic toxicity (*)	96 hr LC50 Fathead Minnow (#) <i>Pimephales promelas</i>	acute toxicity	chronic toxicity	96 hr LC50 Bluegill <i>Lepomis macrochirus</i>	acute toxicity	chronic toxicity	96 hr LC50 Largemouth Bass <i>Micropterus salmoides</i>	acute toxicity	chronic toxicity	96 hr LC50 Rainbow Trout (#) <i>Oncorhynchus mykiss</i>	acute toxicity	chronic toxicity	96 hr LC50 Channel Catfish <i>Ictalurus punctatus</i>	acute toxicity	chronic toxicity
2,4-D	25,000 (7)	8333	1250	133,000 (7)	44333	6650	180,000 (8)	60000	9000	-	-	-	100,000 (4)	33333	5000	-	-	-
	-	-	-	-	-	-	900 (48 hr) (6)	-	-	-	-	-	110,000 (7)	36667	5500	-	-	-
ametryn	28,000 (7)	9333	1400	-	-	-	4,100 (4)	1367	205	-	-	-	8,800 (4)	2933	440	-	-	-
atrazine	6900 (7)	2300	345	15,000 (7)	5000	750	16,000 (4)	5333	800	-	-	-	8,800 (4)	2933	440	7,600 (4)	2533	380
bromacil	-	-	-	-	-	-	127,000 (7)	42333	6350	-	-	-	36,000 (7)	12000	1800	-	-	-
DDD, p,p'	3,200 (6)	1067	160	4,400 (1)	1467	220	42 (1)	14	2.1	42 (1)	14	2.1	70 (1)	23.3	3.5	1,500 (1)	500	75
DDE, p,p'	-	-	-	-	-	-	240 (1)	80	12	-	-	-	32 (1)	10.7	1.6	-	-	-
DDT, p,p'	-	-	-	19 (5)	6.3	0.95	8 (5)	2.7	0.4	2 (5)	0.7	0.10	7 (5)	2.3	0.35	16 (5)	5.3	0.8
dieldrin	-	-	-	16 (5)	5.3	0.80	8 (4)	2.7	0.4	-	-	-	10 (5)	3.3	0.5	4.5 (5)	1.5	0.23
diuron	1,400 (7)	467	70	14,200 (7)	4733	710	5,900 (4)	1967	295	-	-	-	5,600 (4)	1867	280	-	-	-
endosulfan	166 (7)	55	8	1 (1)	0.3	0.05	1 (1)	0.33	0.05	-	-	-	1 (1)	0.33	0.050	1 (1)	0.3	0.05
	-	-	-	-	-	-	2 (3)	0.67	0.10	-	-	-	3 (2)	1	0.15	1.5 (7)	0.5	0.08
	-	-	-	-	-	-	-	-	-	-	-	-	1 (3)	0.33	0.050	-	-	-
	-	-	-	-	-	-	-	-	-	-	-	-	0.3 (5)	0.10	0.015	-	-	-
ethoprop	93 (7)	31	4.7	-	-	-	-	-	-	-	-	-	13,800 (4)	4600	690	-	-	-
hexazinone	151,600 (7)	50533	7580	274,000 (4)	91333	13700	100,000 (7)	33333	5000	-	-	-	180,000 (7)	60000	9000	-	-	-
metalaxyl	28,000 (7)	9333	1400	-	-	-	139,000 (7)	46333	6950	-	-	-	132,000 (7)	44000	6600	-	-	-
norflurazon	15,000 (7)	5000	750	-	-	-	16,300 (7)	5433	815	-	-	-	8,100 (7)	2700	405	>200,000 (4)	>67,000	>10,000
prometon	-	-	-	-	-	-	40,000 (5)	13333	2000	-	-	-	12,000 (5)	4000	600	-	-	-
simazine	1,100 (7)	367	55	100,000 (7)	33333	5000	90,000 (4)	30000	4500	-	-	-	100,000 (7)	33333	5000	-	-	-
trifluralin	625 (7)	208	31	105 (7)	35	5	60 (4)	20	3	75 (7)	25	4	30 (4)	10	1.5	210 (7)	70	11

(\*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC50 is the lowest value which has been determined for a species significant to the indigenous aquatic community.

(#) Species is not indigenous. Information is given for comparison purposes only.

- (1) Johnson, W. W. and M.T. Finley (1980). Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. U.S. Department of the Interior, Fish and Wildlife Service Resource Publication 137. Washington, DC.
- (2) U.S. Environmental Protection Agency (1977). Silvicultural Chemicals and Protection of Water Quality. Seattle, WA. EPA-910/9-77-036.
- (3) Schneider, B.A. (Ed.) (1979). Toxicology Handbook, Mammalian and Aquatic Data, Book 1: Toxicology Data. U.S. Environmental Protection Agency. U.S. Government Printing Office. Washington, DC. EPA-5400/9-79-003
- (4) Hartley, D. and H. Kidd. (Eds.) (1987). The Agrochemicals Handbook. Second Edition, The Royal Society of Chemistry. Nottingham, England.
- (5) Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsea, MI.
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- (7) U.S. Environmental Protection Agency (1991) Pesticide Ecological Effects Database, Ecological Effects Branch, Office of Pesticide Programs, Washington, DC.
- (8) Mayer, F.L. , and M.R. Ellersieck. (1986). Manual of Acute Toxicity: Interpretation and Database for 410 Chemicals and 66 Species of Freshwater Animals. United States Fish and Wildlife Service Publication No. 160.

Table 6. Atrazine Desethyl/Atrazine ratio (DAR) data November 2002.

Date	Site	Flow	atrazine ug/l	moles/l	atrazine desethyl ug/l	moles/l	DAR
11/13/2002	S8	N	0.062	2.87456E-10	0.012	6.39551E-11	0.2
11/14/2002	S38B	N	0.8	3.70911E-09	0.09	4.79664E-10	0.1
11/18/2002	S2	N	0.12	5.56367E-10	0.016	8.52735E-11	0.2
	S3	N	0.1	4.63639E-10	0.025	1.3324E-10	0.3
	S4	N	1.4	6.49094E-09	0.085	4.53016E-10	0.1
11/19/2002	CR33.5T	Y	12	5.56367E-08	1	5.3296E-09	0.1
	S235	Y	0.58	2.68911E-09	0.031	1.65217E-10	0.1
	S78	Y	0.22	1.02001E-09	0.019	1.01262E-10	0.1
	S79	Y	0.56	2.59638E-09	0.036	1.91865E-10	0.1
				Dar	All sites	Flow only sites	No flow sites
				average	0.1	0.1	0.2
				median	0.1	0.1	0.2
				minimum	0.1	0.1	0.1
				maximum	0.3	0.1	0.3